Environmental
Studies
Research
Funds

142

Sheens Associated with Produced Water Effluents - Review of Causes and Mitigation Options

Canada

March 2004

Sheens Associated with Produced Water Effluents – Review of Causes and Mitigation Options

Prepared For: Environmental Studies Research Fund (ESRF-015)

Prepared By: ERIN Consulting Ltd. and OCL Services Ltd.

2002-12-30
Revised 2003-03-10

The correct citation for this report is:
ERIN Consulting Ltd. and OCL Services Ltd. Sheens Associated with Produced Water Effluents – Review of Causes and Mitigation Options 10 March 2003. Environmental Studies Research Funds Report No. 142. Calgary. 46 p.

The Environmental Studies Research Funds are financed from special levies on the oil and gas industry and administered by the National Energy Board for The Minister of Natural Resources Canada and The Minister of Indian Affairs and Northern Development.

The Environmental Studies Research Funds and any person acting on their behalf assume no liability arising from the use of the information contained in this document. The opinions expressed are those of the authors and do not necessarily reflect those of the Environmental Studies Research Funds agencies. The use of trade names or identification of specific products does not constitute an endorsement or recommendation for use.

Published under the auspices of the
Environmental Studies Research Funds
ISBN 0-921652-53-4

Table of Contents

TABLE OF CONTENTS 1

EXECUTIVE SUMMARY 3

RÉSUMÉ 6

INTRODUCTION 9

METHODOLOGY 10

RESULTS 11

Sheen Formation 11
Summary 11
Results 12
Regulations and Sheen Definition 12
Sheens vs. Oil Content of Discharged Water 13
Oil Spill Dynamics 13
Droplet Size 16
Emulsification 18
Solubility 19
Discussion 20

Treatment Technology 21
Summary 21
Results 21
Existing Technologies 21
Biological Technology 22
Mechanical Technology 22
Dispersants 23
Booms 23
Filters/Adsorption Media 24
Skimmers 24
Sensing Equipment 24
Discussion 24

Interviews 26
Summary 26
Results 27
Sheen Occurrence 27
Sheen Causes 27
Sheen Monitoring and Reporting 28
Technologies Used 30
The Influence of Regulations and Future Trends 31
Environmental Effects 32

DISCUSSION 34

Sheen Formation 34

Treatment Technology 34

Interviews 35

CONCLUSIONS AND RECOMMENDATIONS 37

REFERENCES CITED AND SELECTED BIBLIOGRAPHY 39

Tables

Table 1: Oil Droplet Size Rise Rates & Times 16
Table 2: Oil Droplet Size Outcomes 20
Table 3: Selected Treatment Technologies Summary 25

105-05960/

EXECUTIVE SUMMARY

Oil sheens may appear on the sea surface due to the discharge of the produced water accompanying offshore oil and gas production. Sheens can occur despite compliance with Canadian regulatory limits for hydrocarbon concentration. They are primarily of aesthetic concern although sheens may pose non-acute impacts upon ocean flora and fauna present or in contact with the surface microlayer.

A review of literature on oil sheen formation, of internet sources for technology options, and interviews with industry and scientific personnel were carried out to increase understanding of factors involved in sheen formation and to determine options for its prevention and/or mitigation.

Sheens most likely occur when oil droplets entrained in the produced water are large enough to rise to the surface without becoming dispersed in the water column but small enough to avoid breakup due to natural turbulence. Literature suggests this range is 70 to 100+ microns. Some hydrocarbons may also become attached to metal flocs or come out of solution due to temperature changes and rise to the surface. Favourable (calm) weather conditions, sufficient light, and appropriate viewing angle are necessary for sheen observations (a minimum of one micron). Oil composition may also contribute to ease of sheen formation.

Of the ten environmental personnel attached to oil and gas companies who were interviewed for the study, none regarded sheens as cause for concern in themselves because of the rapid evaporation/dissolution and degradation of sheens in the ocean environment. Rather, sheens were viewed as an indicator of possible produced water treatment system failure, of an unintended spill not related to produced water discharge, or arising from cuttings or solids disposal. Additional hydrocarbon testing may be done to check for the cause of sheens.

In the case of the North Sea where sheens may be common at certain platforms, only larger than usual sheens would be investigated. Most companies did some degree of sheen monitoring and tracking. No companies reported regular parameters testing of their produced water beyond hydrocarbons as specified by applicable guidelines or regulations, apart from one company which checked salinity and density as well. No companies had participated in research into environmental impacts of sheens specifically.

Primary consideration for produced water treatment technology includes space and weight due to limitations on production platforms, performance, and reliability/ease of maintenance. Technologies standard within the industry include mechanical units such as separators, plate coalescers, air flotation units and hydrocyclones (in preference to centrifuges). These operate on the basis of density differences between the brine and associated hydrocarbons. Solids removal is also performed in separation units. Chemical treatment to flocculate or coagulate hydrocarbons may also be practiced.

Adsorbents can take levels of hydrocarbons to below detection limits but are typically confined to platforms with low flow rates due to the cost of sorbent material (e.g. carbon, clay, or synthetic materials), replacement/regeneration and throughput limitations. Research and development is ongoing in the area of filters, membranes and ultramembranes but these are not practical for technical reasons at this time. Likewise, bioremediation of produced water contamination has so far been confined to use on shore due to high residence time requirements (which reduce throughput capacity) of current process designs.

Techniques which might be used to deal with sheens after or as they occur include booms and dispersants, however the low frequency and duration of sheening in the open water off the Canadian East Coast is unlikely to warrant extensive use of these measures. Agitation to reduce droplet size prior to discharge or to break up sheens should be considered.

The frequency and significance of sheens still needs to be evaluated. Sheen formation cannot be predicted from information available at this time. The impacts of these very small volumes of hydrocarbons beyond visual impacts are also unclear.

It is recommended that ESRF:

1. Work with various Canadian offshore operators to institute a three-month program to evaluate the frequency and significance of sheens. The proposed monitoring program should include reporting of (a) the estimated size of the sheen, (b) the concurrent concentration of petroleum hydrocarbons in the discharge produced brine; (c) the influence of trace metals within the brines on the visualization of the sheens and (d) the concentration of the total suspended solids in the produced brine.
   Alternative analytical techniques should be trialed to determine if their results for petroleum range hydrocarbons correlate better with the propensity of produced water to produce sheens. It is suggested that existing on-board weather/bird/wildlife observers could be readily trained to check for sheen formation and to correlate observations with other data. It may also be necessary for the rig operators to augment their existing discharge monitoring activities.

2. Work with industry to study of the environmental impacts of sheens, particularly impacts to seabirds and plankton within the upper 1 cm surface layer, should be completed. Issues to be evaluated should include effects on seabirds of low-level oiling of feathers, interruption of feeding, and scope for growth. The results of such studies would assist decision-makers with respect to imposing management controls on sheen formation and the concurrent discharge of petroleum hydrocarbons within produced waters.

3. Work with industry to (a) evaluate and implement new technologies for the removal of petroleum hydrocarbons from produced brines, including bioremediation and filtration and (b) evaluate and implement methods of

discharging produced waters in such a manner as to impede the formation of sheens (e.g. by imparting more energy during discharge).

RÉSUMÉ

Le rejet de l'eau produite dans l'extraction en mer du pétrole et du gaz peut créer des taches d'huile à la surface de la mer. Il peut s'en former même quand on se conforme aux limites réglementaires canadiennes concernant les concentrations d'hydrocarbures. Les taches sont surtout préoccupantes du point de vue esthétique, mais elles peuvent avoir des impacts non aigus sur la flore et la faune océaniques avoisinantes ou en contact avec la microcouche de surface.

Un examen de la documentation sur la formation des taches d'huile et des sources traitant des options technologiques sur l'Internet ainsi que des entrevues avec des représentants de l'industrie et des chercheurs ont été effectués pour mieux comprendre les facteurs en cause dans la formation des taches et examiner comment l'empêcher et/ou l'atténuer.

Les taches apparaissent plus probablement quand les gouttelettes d'huile entraînées dans l'eau produite sont suffisamment grosses pour monter à la surface sans se disperser dans la colonne d'eau, mais suffisamment petites pour ne pas se fractionner sous l'effet de la turbulence naturelle. D'après la documentation, cette taille devrait se trouver entre 70 et 100+ micromètres. Certains hydrocarbures peuvent également se fixer à des flocons de métal ou être extraits de la solution sous l'effet d'un changement de température et monter à la surface. Des conditions météorologiques favorables (calmes), un éclairage suffisant et un angle de vue approprié sont nécessaires pour voir les taches (un minimum d'un micromètre). La composition de l'huile peut également contribuer à faciliter la formation des taches.

Parmi les dix personnes appartenant à des sociétés pétrolières et gazières qui ont été interviewées pour l'étude, aucune ne jugeait les taches préoccupantes parce qu'elles s'évaporent ou se dissolvent rapidement et se dégradent dans l'environnement océanique. Les taches sont plutôt perçues comme des indicateurs d'une défaillance possible du système de traitement de l'eau produite ou d'un déversement accidentel non lié au rejet de l'eau produite ou provenant de l'élimination des déblais ou de corps solides. D'autres essais sur les hydrocarbures pourraient être effectués pour déterminer la cause de ces taches.

Dans la mer du Nord où les taches d'huile peuvent être courantes à certaines plates-formes, seules les taches plus étendues que la moyenne feraient l'objet d'une investigation. La plupart des entreprises ont surveillé et suivi les taches à un certain degré. Aucune n'a déclaré avoir mesuré d'autres paramètres que ceux des hydrocarbures précisés dans les lignes directrices ou les règlements, sauf une qui a également mesuré la salinité et la densité. Aucune entreprise n'a participé à des recherches spécifiques sur les impacts environnementaux des taches d'huile.

Les principaux facteurs pris en compte dans la technologie du traitement de l'eau produite sont l'encombrement et le poids en raison des limites imposées par les plates-formes de production, le rendement, et la fiabilité ou la facilité d'entretien. Les technologies standard dans l'industrie comprennent des unités mécaniques comme les séparateurs, les coalesceurs, les unités d'aéroflottation et les hydrocyclones (de

préférence aux centrifugeuses). Ces appareils utilisent la différence de densité entre la saumure et les hydrocarbures connexes. L'extraction des solides est également effectuée dans des unités de séparation. On peut aussi utiliser un traitement chimique pour floculer ou coaguler les hydrocarbures.

Les adsorbants peuvent abaisser les concentrations d'hydrocarbures sous les limites de détection, mais ne sont généralement utilisés qu'aux plates-formes à faible débit en raison de leur coût (carbone, argile ou matériaux synthétiques), de la nécessité de les remplacer ou de les régénérer, et de leurs capacités limitées. Des travaux de recherche et de développement se poursuivent dans le domaine des filtres, des membranes et des ultramembranes mais, à l'heure actuelle, ils ne sont pas pratiques pour des raisons techniques. De même, la biorestauration de l'eau produite contaminée n'a été utilisée que sur la terre ferme jusqu'ici en raison de la longue durée de résidence (qui réduit la capacité de traitement) requise par les procédés actuels.

Les techniques qui pourraient être utilisées pour circonscrire les taches d'huile après ou durant leur apparition comprennent les barrages flottants et les dispersants, mais la rareté et la brièveté de ces taches dans les eaux libres de la côte est du Canada ne pourront probablement pas justifier une utilisation intensive de ces mesures. Il faudrait examiner la possibilité d'utiliser l'agitation pour réduire la taille des gouttelettes avant le rejet ou pour décomposer les taches.

La fréquence et l'importance des taches d'huile restent toujours à déterminer. La formation des taches ne peut être prédite avec l'information disponible actuellement. L'aspect visuel mis à part, les impacts de ces très petits volumes d'hydrocarbure sont également inconnus.

On recommande que le FEE :

4. travaille avec diverses entreprises canadiennes d'exploitation en mer pour instituer un programme de trois mois visant à évaluer la fréquence et l'importance des taches d'huile. Le programme de surveillance proposé devrait comprendre la déclaration a) de la taille approximative des taches, b) de la concentration concomitante des hydrocarbures de carbone dans la saumure produite par le rejet, c) l'effet des métaux à l'état de traces dans la saumure sur l'apparence des taches et d) la concentration du total des particules en suspension dans la saumure produite.
   D'autres techniques analytiques devraient être mises à l'essai pour déterminer si les résultats pour les hydrocarbures sont mieux corrélés avec la propension de l'eau produite à créer des taches. On croit que les observateurs des conditions météorologiques, d'oiseaux ou de la faune pourraient rapidement être formés pour déceler la formation des taches et corréler leurs observations avec d'autres données. Il pourrait également s'avérer nécessaire pour les exploitants des plates-formes d'accroître leurs activités de surveillance des rejets.

5. termine le travail entrepris avec l'industrie pour étudier les impacts environnementaux des taches d'huile, particulièrement les impacts sur les oiseaux

de mer et le plancton dans une couche de 1 cm sous la surface. Les questions à examiner devraient inclure les effets sur les oiseaux de mer des minces dépôts d'huile sur les plumes et de l'interruption de l'alimentation, ainsi que les perspectives de croissance. Les résultats de ces études aideraient les décideurs à imposer des contrôles de gestion sur la formation des taches d'huile et le rejet concomitant d'hydrocarbures de pétrole dans l'eau produite.

6. travaille avec l'industrie pour a) évaluer et mettre en œuvre de nouvelles technologies pour extraire les hydrocarbures de pétrole des saumures produites, y compris la biorestauration et la filtration, et b) évaluer et mettre en œuvre des méthodes de rejet des eaux produites de façon à empêcher la formation de taches d'huile (p. ex. par un plus grand transfert d'énergie durant le rejet).

INTRODUCTION

As with most oil and gas production, offshore production produces salt water brines, commonly known as produced waters or formation waters, as a waste product of the production. These brines are most often disposed of by pumping them after treatment to remove petroleum hydrocarbons into the sea around the production platforms. Small quantities of petroleum hydrocarbons are still contained in the discharged brines.

Although strict regulatory guidelines are in place for the amount of hydrocarbons carried over in the brines (National Energy Board, Canada-Newfoundland Offshore Petroleum Board, Canada-Nova Scotia Offshore Petroleum Board, 2002), occasionally, sheens may form at the ocean surface near the production platforms. This is despite industry precautions to prevent excess petroleum hydrocarbons in the brines and despite industry performance monitoring.

A number of concerns have been raised with respect to sheen formation from the disposal of produced brines. These range from visual appearance of the sheens to potential impacts on plankton and birds.

Little is known or understood about the reasons why sheen form or how often they appear. The Environmental Research Studies Fund (ESRF) contracted ERIN Consulting Ltd. of Regina and OCL Services Ltd. of Dartmouth to review sheen formation from the disposal of produced brines.

The primary objectives for this study were:

- To review why and how sheens form
- To review technology used to prevent sheen formation
- To determine frequency and occurrence of sheens

METHODOLOGY

The methodologies used to complete this study included literature reviews, internet reviews, discussions with technology vendors and interviews with offshore operators. Specific field observations or sampling were not included as part of the study. The study was to rely on existing literature, research and operator experience.

The methodologies worked reasonably well. Although initial literature searches for the causes of sheen formation proved difficult, persistent searches did yield a large body of research on sheens and their causes.

Technology reviews identified a relatively small number of produced water treatment technologies in use or ready for use. Most of this technology is currently employed for removal of hydrocarbons from water at this time.

The operator interviews were not at first well received. This changed, as operators understood the reasons why the information was being collected. Sufficient information was gathered during the interviews to complete this report. Although we requested specific data on oil in water concentration and how they related to the appearance of sheens, few operators had such correlations and most operators were reluctant to supply data for the report. Thus, the section on observations is largely based on incidental observations from operators. Information from international researchers on sheen formation is included in the report.

RESULTS

The results of the reviews and interviews are discussed below. The results and subsequent sections are divided into three parts: sheen formation, technology and interviews. These sections summarize the results obtained. More detail and references are included in the appendices.

Sheen Formation

Summary

Applicable guidelines and reports of performance indicate average petroleum hydrocarbon concentrations of 20 to 40 ppm in produced water may be associated with sheens. Effluent testing methods used by the industry to satisfy regulations may not be able to adequately detect some types of hydrocarbons associated with produced waters. Thus varying concentrations of polar hydrocarbons, or hydrocarbons at the lower molecular weight end of the C_4-C_{30} range might be released with the produced water discharge and become a factor in sheen formation.

The review of spill and dispersant literature indicates that petroleum hydrocarbon droplet sizes in produced water effluent could be a factor in sheen formation. If middle range droplets are present in the ocean discharges these droplets may float to surface and appear as sheens, particularly at times of calm sea state and wind. Particles must be large enough to have sufficient upward velocity, yet small enough to avoid breakup due to turbulence.

Assuming the platform discharge to be an oil-in-water (i.e., a reverse) emulsion with some dissolved hydrocarbons, it appears that the decrease in temperature from the produced water treatment processes to the ocean may affect sheen formation:

- Viscosity and surface tension increase as temperature lowers, raising the energy required to break up oil droplets.
- Solubility decreases due to lowered temperatures could make hydrocarbons dissociate from the produced water when it is cooled by dilution with colder ocean waters, such as would be encountered in eastern Canada.

The literature is inconclusive as to whether asphaltenes and wax content may stabilize oil-in-water emulsions, in addition to water-in-oil emulsions. Suspended solids nearly always contribute to elevated hydrocarbons in produced water effluent. The effect of solids on emulsions is complex: most sources agree that solids can stabilize emulsions, however residual (heavy) ends are expected to sink faster in waters with increased concentrations of suspended solids. In contrast, research after the *Exxon Valdez* spill suggests that fine-grained particles can detach oil from sediments and the resulting oil-particles float to surface in sheltered areas.

Provided environmental conditions like wind and wave turbulence are favourable, seemingly minute concentrations of hydrocarbons may accumulate on the surface. Given the continuous discharge of produced water, 'residence time' in the ocean may allow for more oil/water separation at sea than during typical treatment on offshore platforms. Current tests do not differentiate between dissolved and undissolved hydrocarbons within the sample, so that the effect of dispersed hydrocarbon versus dissolved petroleum hydrocarbon within the produced water discharged cannot be easily estimated.

In summary the factors influencing sheen formation include:

- Oil droplet size
- Type of hydrocarbon in the produced water
- Ocean temperature
- Ocean surface conditions
- Asphaltene and/or wax concentrations
- Amount of solids in the produced water

Sheen is also a visual phenomenon. The relative position of a viewer to the ocean surface will be critical in perception of a sheen, assuming "correct" environmental conditions of light, surface conditions, etc.; i.e., the concentrations and types of hydrocarbons within the effluent may be essentially "constant", but the perception of sheen is likely to be very episodic.

Results

Regulations and Sheen Definition

New guidelines for the Canadian offshore industry (National Energy Board, Canada-Newfoundland Offshore Petroleum Board, Canada-Nova Scotia Offshore Petroleum Board, Offshore Waste Treatment Guidelines, 2002) require testing of produced water every 12 hours. The 24 hour arithmetic averages of dissolved oil concentrations are to be 60 mg/L or less and the rolling weighted 30 day average is not to exceed 40 mg/L, for existing facilities. The latter limit decreases to 30 mg/L by the end of 2007, while new facilities must hit this target as of the coming into force of the guidelines. Produced sand should be re-injected or treated to reduce hydrocarbon content to the lowest level practicable.

Visible sheens are not explicitly mentioned in the Canadian offshore guidelines cited above. In contrast, in the US, these may be cause for penalties and a visible sheen testing methodology, not without some problems in replication/repeatability among testers (Weintritt et. al., 1993), is specified. The National Oceanic and Atmospheric Administration defines oil sheens as oil layers less than 2 or 3 microns (thousandths of a millimeter) in thickness. Colourful sheens occur when the thickness approaches that of visible light wavelengths (less than a micron). At the one micron thickness, films will disappear within 24 hours, and within 20 to 60 minutes for films 10 times thinner

(Miyahara, 1987). Black oil describes a thicker film of oil, perhaps a millimeter (1000 microns) thick. Emulsification of a slick, where water droplets become entrained in the oil slick, usually appears dark brown or tan.

Sheens vs. Oil Content of Discharged Water

Dan Byers, a chemical company (ONDEO Nalco) representative serving the offshore industry in 1996 in the Gulf of Mexico, also recalled that sheens were common (pers. comm., 2002). He thought applicable regulations at the time were 20 ppm. and that the presence of iron was a contributing factor to sheens.

Jonathan Wills (2000) reported that visible sheens can occur at 25 ppm on the sea in calm conditions. Apparently, faint sheens downwind of offshore platforms are routine in the North Sea, where effluent concentrations reportedly average 22 ppm, below the regulatory limit of 40 ppm averaged monthly (UKOAA, 2000). In contrast, the onshore Sullom Voe treatment facility in the Shetlands treats oily waters from offshore production to less than 4 ppm. Wills maintained that he had never witnessed a sheen there despite daily observations a few years ago. The Sullom Voe facility had rare peaks around 15 ppm (2002). It was also discharging into a tidal sound with strong currents, which provide fast mixing with ocean water, unlike seabed areas with slower currents.

The testing methodology for produced water hydrocarbon concentrations cited in the Canadian guidelines indicates that an oil and grease partition method is to be followed by a test to quantify the petroleum hydrocarbons range within the oil and grease. While the oil and grease test can accurately measure most of the more volatile hydrocarbons outside of the gasoline fraction, it can underestimate the light end of the diesel fraction (Gavin Plosz, Enviro-Test Laboratories, pers. comm., 2003) as well as heavier hydrocarbons, which do not readily dissolve in the trichlorotrifluorethane solvent used. The second test uses silica gel to remove fatty acids so as to limit the test to the petroleum hydrocarbon range (typically specified as C_4-C_{30}). It removes polar compounds (American Public Health Association, American Water Works Association, Water Environment Federation, 1992), which are typically associated with plant decay and non-petroleum fractions.

Purge and trap techniques for gas chromatography with flame ionization detection (EPA 5030/8015 P&T GC-PID) might better evaluate the total volatile hydrocarbons (C_4-C_{10}) in water. Hexane solvent with a shake method similar to the oil and grease method (EPA 3510/8000 GC-FID) could provide a superior method of determining the total extractable hydrocarbon range (C_{11}-C_{30}).

Oil Spill Dynamics

The simplest explanation for oil sheen formation is that oil floats on water. This is because oil is typically appreciably lighter than water. Measured as specific gravity (density relative to water at a given temperature), crude oils range from 1 to less than 0.80 s.g. and condensate can be less than 0.75 s.g. (McCain, 1983); seawater is slightly

greater than pure water, at 1.02 s.g. (Ayers and Parker, 2001). Palczynski (1987) measured density decreases of 0.7% per °C rise, on average for four crude oils.

While no studies have been obtained which specifically address the issue of sheen formation from the standpoint of discharged water without free oil, there is a large body of oil spill literature. These studies almost invariably start with the spilled hydrocarbons as free liquid on the surface of the water, and then go on to discuss the fate of the resulting oil slicks. Nevertheless, the oil spill literature provides information relevant to the problem of oil sheen formation.

Oil slicks spread, at first, mainly under the influence of gravity, due to the specific gravity differences noted above. Various mathematically and empirically based formulas exist for oil slick spreading. For example, Antunes de Carmo and Costa (2000) used the following spreading formula rating R (radius) and *t* (time) in their numerical spill model:

$$\frac{d^2R/dt^2}{} = \frac{3\,g\,V\,\Delta}{2\,\pi\,R^3} + \frac{3\,\pi\,\sigma\,R}{\rho_o\,V} + \frac{1}{R}(dR/dt)^2 - 2.628\,\frac{\rho_w\,\nu_w^{1/2}}{\rho_o\,V}(R\,dr/dt)^{1.5} - 3\,\nu_o\,\frac{1\,dR/dt}{R^2}$$

where V = volume, ν_o and ν_w = oil and water kinematic viscosity respectively, ρ_o and ρ_w = oil and water density respectively, σ = mean surface stress, g = gravitational acceleration and $\Delta = (\rho_w - \rho_o) / \rho_w$.

Palczynski (1987) characterizes slicks as being dominated successively by gravity, viscous, and surface tension regimes. The higher the oil's viscosity and surface tension, the slower the oil slick will spread:

- Viscosity is a measure of a liquid's resistance to flow. The higher the viscosity, the thicker it appears and the more resistant it is to flow for a given force. The heavier hydrocarbon mixtures tend to be more viscous, and viscosity is highly dependent upon temperature with high temperatures lowering viscosity (charts exist to estimate viscosity for a given oil density, using an exponential relationship). Palczynski (1987) measured viscosities at different temperatures for four crude oils (0.79 to 0.90 specific gravities and pour points {temperature above which the oil will flow} of -53 to -2°C). Viscosity decreases were different for each oil, but large over the temperature range studied: they varied from 3 to 600 Centistokes (Cst) at 5°C and from 2 to 90 Cst at 40°C.

- Surface tension measures the energy required to increase the surface area of a liquid. Higher surface tension will tend to make round droplets (with a small surface or skin area) instead of a thin film (large skin area) at its interface with another material. Palczynski also found that surface tension for the crudes studied decreased with higher temperature at an average rate of 0.2% per °C, based on four crude oils.

Palczynski's work with the above mentioned four crude oils found one dimensional spreading speed (e.g. change in length of a slick over time) increased 1% for each 1°C

increase. For example, the length of the slick grew from 11 cm at 2 seconds after spill, to over 200 cm in less than 20 seconds at 30°C; the slick grows from 22 cm at 3 seconds to only 150 cm after more than 20 seconds at 10°C (laboratory simulated calm conditions). Miyahara (1987) noted that spills of lighter products like gasoline form thin slicks and sheens the fastest. Once a slick has thinned out, even a crude oil will spread very quickly.

Consistent with these factors, the European Commission's Community Impact Reference System gathers a variety of oil characteristics to help stakeholders estimate oil spill impacts (n.d. [2002]). Along with density, pour point and viscosity, wax and asphaltene contents (which can cause slicks to become water-in-oil emulsions or "mousse") are specified. As well, qualitative estimates of volatility (which reflects an oil's tendency to evaporate), solubility, "stickiness" and response to dispersants (which promote the break up of slicks through droplet distribution into the water column) are included.

Weathering, which involves the loss of light ends due to evaporation, photo or chemical breakdown or dissolution, causes the viscosity and specific gravity of the remaining hydrocarbon mixture to increase. Light ends are volatile and will readily evaporate from the surface of an oil spill. The lower a hydrocarbon's molecular weight and the more polar its structure, the more easily it will dissolve into the water column. Aromatic (ring structure) hydrocarbons are generally more soluble than alkanes (straight chain). For example, vapour pressure (a measure of volatility) and solubility range from 90 mm Hg and over 1 mg/L respectively for benzene, a mono-aromatic that is a primary constituent of gasoline, to 0.00001 mm Hg and less than 0.001 mg/L for much heavier six ring hydrocarbons (Vershueren, 1996).

Many spill models have been used to simulate the effects of actual or hypothetical spills. To do this well, other ocean/climate factors, which can have large impacts on spill behavior, must be taken into account in addition to the oil's properties. For example, waves can increase dispersion and the formation of emulsions; wind influences the direction and speed of advection along with current; salts may change solubilities; low temperatures will increase viscosity as noted above and in doing so decrease biodegradation rates; silt can attach to oil and help sink residual ends which are nearly as dense or more dense than water; etc.

French McCay and Payne (2001) discuss a comprehensive spill impact model (SIMAP) which takes into account spreading, entrainment, dissolution, evaporation and dosage on marine life. Properties including boiling point, vapour pressure, molecular weight, solubility and octanol partition coefficient (as a surrogate for toxicity) were established for seven pseudo components of crude oil – volatile, semivolatile, or low volatility aromatics (cyclic or ring hydrocarbons) and aliphatics (straight chain hydrocarbons); and residual aromatics and aliphatics. Surface and subsurface oil releases can be simulated. The model quantifies the volume of "resurfacing…submerged oil droplets", depending on ocean conditions and a specified diameter (French McCay, 2002, p. 2). They note that above wind speeds of 12 knots, waves cause oil on surface to be entrained into the water column, with larger particles resurfacing at lower speeds.

Droplet Size

The treatment technology literature focuses upon oil droplet size because it is the principle behind typical oil/water separation practice. Briefly, the larger the oil droplet, the faster it will rise to the surface of the water or otherwise be separated from the water because of density differences. Stoke's equation calculates the highest speed of an oil droplet's ascent, based on its size and density, and the density and viscosity of the water which cause a drag on the droplet opposing its motion upwards). Table 1 below shows time to rise one meter for a crude oil (adapted from Lunel, 1995).

Table 1: Oil Droplet Size Rise Rates & Times

DIAMETER (micron)	RISE VELOCITY (cm/min)	TIME to rise 1 meter (min)
10	0.0	3330
20	0.1	760
30	0.3	340
40	0.5	190
50	0.8	120
70	1.6	62
80	2.1	48
100	3.3	30
150	7.2	14
200	13.2	8
300	29.4	3
400	52.2	2
500	81.6	1

Depending on the distribution of oil droplet sizes in the produced water, a given residence time (in a tank or in the ocean) may separate out a specific percentage of oil which appears as a slick or sheen on the water surface. This phenomenon, buoyancy, is just one of five forces which act on an oil droplet released into the ocean:

1. Tide
2. Wind
3. Waves
4. Diffusion
5. Buoyancy

While the first three can have strong effects on horizontal spreading, the last three are more important:

- Based on oil droplet sizes dispersed within the water column, Lunel concluded particles over 70 microns could be considered to be suspended, not dispersed, i.e.

prone to buoyant forces and likely to rise to surface. Those under 70 microns were governed by vertical diffusion, not buoyancy. His research on dispersant effectiveness noted that micro-scale turbulence or shear forces are what break down droplets into sizes small enough to disperse effectively. Interestingly, the surfactants differed only in the amount of oil they brought into the water column: resulting distribution sizes were the same, ostensibly due to the breakup mechanism provided by the ocean: distribution peak at about 22 microns, 99% of the particles were less than 70 microns (80-90% of the volume), 90% < 45 microns (50% of the volume). As compared to Lunel, Fingas et. al. (1991) suggest a somewhat (right-shifted) distribution of diameters in stable dispersions after surfactant use, which they reported as a Volume Mean Diameter (VMD) of 30 microns, i.e. 50% of the oil volume was represented by droplets 30 instead of 45 microns and under. French McCay and Payne (2001) simulated dispersant application with an oil droplet distribution smaller than 25 microns, and in their simulation for a spill near Galveston Bay with an ocean depth of 15 m, only a "small fraction" later resurfaced. In modeling Orimulsion, with a density very close to that of water, in an environment with some turbulence, 70 microns is noted as small enough to keep droplets entrained in the water column (French McCay and Whittier, 2002).

- In a slightly different way, Li and Garrett (1998) back up Lunel's finding. They maintain that depending on the Reynolds number of an oil droplet (which is determined from droplet diameter and velocity as compared to viscosity) and the energy of the wave regime, either pressure or mainly viscous shear forces will break up droplets. Under normal or strong wave conditions (0.1 to 10 m^2/s^3) which occur close to surface, pressure is the dominant breakup force, causing particle sizes greater than about 100 microns to breakup. They note that the use of dispersants to reduce viscosity by 20 times would reduce the Reynolds number, so that shear forces would dominate in these wave conditions. Maximum particle sizes would be limited to an order of magnitude of ten (microns). With buoyancy rise speeds of 0.01 to 0.001 cm/s, droplets in this range would be expected to disperse (remain in the water column) rather than rise to the surface. They also cite research that links viscosity to persistence of larger oil particles, French McCay and Payne's model reportedly also takes this relationship into account (2002).

- Osamor (1981, p. 43) stated that droplets greater than 75 microns "are no longer neutrally buoyant" but tend to flocculate or coalesce and rise to surface. Turbulent conditions cause smaller particle size distributions, with larger droplets having a higher chance of breaking. Osamor reported a formula for determining the critical droplet size (involving oil and water density and interfacial tension) – one that would be readily broken by turbulent mixing. This follows from the relationship between the wave energy required to break up a droplet and the surface area of the droplet multiplied by its surface tension. Substituting typical densities and crude/salt water interfacial tensions ranging from 17 to 29 N/m reported by Osamor, values in the tens of microns were obtained for this study.

Emulsification

Reverse emulsification may have a bearing on the fate of oil droplets discharged with produced water. A stable oil-in-water emulsion "has no tendency to flocculate or coalesce" – this is what dispersants try to achieve (Osamor, 1981, p. 54). An emulsion is the state of the oil droplets / water mixture prior to the oil becoming dissolved, degraded, adsorbed onto particles and sinking to form sediment, etc.

If substances with both hydrophilic and oleophilic ends form coatings on the oil droplets, they can make very stable oil-in-water emulsions that resist combining with other droplets. Hrudey and Kok (1987) note that electrical barriers e.g. polar molecules along oil droplets or steric (physical) barriers can stabilize oil-in-water emulsions. The latter can be caused by various surfactants (surface active substances) or by clays or organic macromolecules attached to the oil droplet surface. Mechanical properties (intermolecular forces between different surfactants that can form strong coatings) and surfactant properties (which reduce the interfacial tension and therefore the advantage to coalesce) can make coalescence and concomitant emulsion breakup less likely even if droplets come into contact with each other.

Allen and Roberts (1993) note that partially oil-wet clays/fines of less than 0.5 microns are significant stabilizers. Research by Bragg and Yang (1995) supports the idea of particulates assisting sheen formation. They found clay-oil flocculations were responsible for the natural cleansing of sediments in sheltered areas after the Exxon Valdez spill, e.g. within non-abrasive subtidal zones. These particles of approximately 50 microns and larger floated to the surface. Lab experiments showed this phenomenon happened best when mineral (clay) particles were small.

As alluded to in the previous section, the EC tracks the asphaltene and wax content of hydrocarbons commonly transported in European waters, but explain that this is because these constituents favour formation of water-in-oil emulsions. When these occur in a surface slick, they are called mousse, entraining as much as 80% water by volume. Dunstan et. al. concurs with the EC document, stating that asphaltenes and "fine earthy material" promote water-in-oil emulsions (1938, p. 1062) more so than oil-in-water emulsions. Lee (1999), in discussing oil-in-water emulsions, asserts sufficient amounts of specific polar compounds like nickel porphyrins (part of the asphaltene fraction) are necessary, without which particles and waxes cannot cause stable emulsions.

Solids carry over from produced water treatment is one mechanism for entry of higher than normal levels of hydrocarbons to be discharged to the ocean. A study of produced brine from offshore crude production platforms in Louisiana failed to find a significant correlation between suspended solids and produced water effluent, however this was attributed to possible problems with analytical techniques (Jackson et. al., 1981).

Solubility

Solubility is the final factor identified as having a possible role in sheen formation. If hydrocarbons are dissolved and therefore not separated during the produced water treatment process, which relies on density differences, they could be a source of oil for a sheen. Treatment temperatures are often elevated (over 40°C) to enhance performance of oil/water separation technology; whereas surface ocean temperatures in Eastern Canada are near freezing much of the year. Ayers and Parker (2001) reported dilution modeling for Hibernia had used values of 78°C for discharge water temperature (for the first 10 years of production at 339 m^3/hr). They also noted that dissolved organics usually account for 5 to 30 ppm of produced waters, although levels can reach over 200 ppm.

Solubility information is limited as to temperature dependence. Based on data for a handful of specific hydrocarbons, it appears that differences from 5 to 20°C are on the order of 20%. For example, Norman Wells crude is reported as 20 mg/L at 5°C, 25.5 mg/L at 22°C (Shiu et al., 1990). Osamor notes that there are a large number of methodologies for testing solubility, which can produce widely varying figures. For example, residence time may significantly affect results. An early Canadian study found a medium Western crude took two days to reach 90% of its peak dissolved level of volatiles, a dissolution rate of 8915 mg/m^2/day (Lu and Polak, 1973).

Moreover, there may be different forms of solubility responding to different environmental factors. Osamor noted three degrees of aggregation have been theorized for substances in solution:

1. true solution
2. colloid and molecular aggregations less than 1 micron
3. droplets over 1 micron.

Osamur also described a theory of "accommodation" where hydrocarbons can become dissolved beyond what would be expected by their vapour pressure and ideal solution assumptions. Some correlations have been derived for different types of hydrocarbons relating this solubility to molar volume, molecular weight, and the calculated size of the "solvent cavity" (1981, p. 31). Mixtures of hydrocarbons in water may increase, decrease or not affect individual solubilities. Osamor noted that salting out effects had been found to be quite limited, in contrast to previous research. Natural surfactants/solubilizers can also affect solubilities, along with the factors above. Dilutions of 100 times within 10 m of platform discharge point have been reported (Ayers and Parker, 2001). This would affect the opportunity for molecules to coalesce so as to become large enough to rise to surface. Thus it is unclear if solubility decreases could be responsible for sheen formation.

Chemical testing such as that done in accordance with the Canadian guidelines cannot determine the relative proportions of truly dissolved oil in water and dispersed (emulsified) oil in water. Dispersed and not dissolved components may be inferred if the test results show high concentrations of low solubility components.

Discussion

Applicable guidelines and reports of performance indicate average oil concentrations of 20 ppm and more in produced water may be associated with sheens. Testing methods used by the industry to satisfy regulations may miss some types of hydrocarbons associated with produced waters. Thus high levels of polar hydrocarbons, or hydrocarbons at the light end of the C_4-C_{30} range might be a factor in sheen formation.

The review of spill and dispersant literature indicates that oil droplet sizes emerging from produced water treatment trains could be a factor in sheen formation. If middle range droplets are present in the ocean discharges, which are large enough to have sufficient upward velocity, yet small enough to avoid breakup due to turbulence, they may float to surface and appear as sheens, particularly on calm days. Table 2 below summarizes findings with respect to oil droplet size.

Table 2: Oil Droplet Size Outcomes

Oil Droplet Size (microns)	Action	Qualifier/ Explanation	Source
<25	Disperse	Modelling of dispersant application	French McCay and Payne
50+	Float to surface	As clay/oil floc in sheltered areas	Bragg
<70	Disperse	Wave shear force keeps droplets smaller than this dispersed.	Lunel, French McCay and Whittier
>75	Rise to surface	Are "no longer neutrally buoyant" if not turbulent conditions, which tend to break up larger particles.	Osamor
100+	Break into smaller particles	In normal/strong wave action.	Li

Viewing the platform discharge as an oil-in-water (i.e. reverse) emulsion with some dissolved hydrocarbons, it appears that the decrease in temperature from the produced water treatment processes to the ocean may affect sheen formation:

- Viscosity and surface tension increase as it gets colder, raising the energy required to break up oil droplets. Emulsification stabilizers may also inhibit particle break-up.

- Solubility decreases due to lowered temperatures could make hydrocarbons dissociate from the produced water when it is cooled by dilution with colder ocean waters.

The literature is inconclusive as to whether asphaltenes and wax content may stabilize oil-in-water emulsions in addition to water-in-oil emulsions. The effect of solids on emulsions is complex: most sources agree that solids can stabilize emulsions, however

residual (heavy) ends are expected to sink faster in silty waters and experience after the Exxon Valdez spill suggests that fines can detach oil from sediments and the resulting particles float to surface in sheltered areas.

Provided environmental conditions like wind and wave turbulence are favourable, seemingly minute concentrations of hydrocarbons may come out of solution or emulsion and accumulate on the surface, given the continuous discharge of produced water. 'Residence time' in the ocean may allow for more oil/water separation at sea than during typical treatment on offshore platforms. Current tests do not differentiate between dispersed and dissolved hydrocarbons within the sample, so that the effect of dispersed oil vs. dissolved oil within the produced water discharged cannot be easily estimated.

It should be noted that treatment equipment is typically sized to remove droplets above a certain diameter in order to reduce oil concentration to a target level. This involves estimating dissolved phase and the distribution of oil droplet sizes in the water initially. Estimates vs. use of laser beam imaging to characterize droplet distribution and centrifuging to separate emulsified vs. dissolved fractions may not be used. In their place, industry rules of thumb would be relied upon. Reducing 1000 ppm oil in water including 6 ppm dissolved oil to the 48 ppm level called for a design removal size of 21 microns, using a straight line distribution with maximum droplet size of 500 microns (Arnold and Stewart, 1999).

Treatment Technology

Summary

Gravity separation coupled with flotation or hydrocyclones is the most widely used technology train; organophillic clay is also being used for gas production facilities where water rates are relatively low. Additional technology in the form of biotreatment or new filters or membranes may become more widely used in the future.

Results

Existing Technologies

Typically, in the offshore oil and gas industry, the most commonly used method for produced water treatment is fundamentally a form of gravity separation, based on the density difference between oil and water. It is generally a multi-step process which may contain any or all of the following: low, intermediate ad/or high pressure gravity separators, skim tank, parallel plate or corrugated parallel plate separator, flotation cell and/or hydrocyclone. These are the technologies of choice in that they save space and deck load, adopt to a wide range of flow rates, have comparatively low cost and their performance is adequate. The drawback of this treatment train is its occasional failure to meet industry standards. Chemical coagulant and flocculation systems may also be

employed. These can improve performance of the other systems by enlarging oil droplet size. Less commonly used technologies at offshore facilities include centrifuges, and steam stripping, for gas production more so than oil.

Dan Byers of ONDEO Nalco has specific experience working with the offshore industry in the Gulf of Mexico. He noted (pers. comm., 2002) that with regulatory requirements in the 20 ppm range, sheens still formed, particularly with high iron content and shallow discharges. In his opinion, problems meeting new more stringent regulations may be a function of older equipment, variable content of solids in the water, and/or the composition of the oil (heavier crude).

Biological Technology

Full-scale biological treatment of produced water from offshore operations is still not widely used. Research continues in this direction with onshore facilities conducting the majority of the activity.

In places such as California, where offshore rigs are relatively close to shore, produced water is piped as far as ten miles to onshore facilities where it is processed. In other areas the use of a companion ship, which docks at or near the rig with the sole purpose of processing water is being implemented. The issues of retention time, volume, and deck load/area remain to be properly addressed, if offshore biodegradation is to become achievable.

Conversely, if sheen forms after the produced water has been discharged, a number of biodegradable, biologically active absorbents have been developed which could be spread on a sheen surface (e.g. PRP®, RamSorb®). Surfactants inoculated with indigenous bacteria are available to reduce droplet size and initiate biodegradation (e.g. PowerClean) but have not been trialed for ocean use. These alternatives may work in theory, although temperatures in Canada's Atlantic Ocean offshore areas would most likely be the limiting factor in biological degradation.

Mechanical Technology

A number of companies including Minox Technology manufacture full-scale oil/water separation equipment reportedly capable of reducing hydrocarbon levels to 10 ppm, while maintaining flow rates of 200 cu m/hour. These systems rely primarily on the principal of density differential as mentioned above, and can be installed either as a complete turnkey operation, or added to existing facilities to enhance treatment.

A number of other companies investigated (e.g., Torr, Axsia Products and ET 1) market systems that can reduce levels to 5 ppm. Although performance is increased with these systems, flow rate is considerably lower (5-50 cu m/hour) as is the case with the Axsia Products package.

Downhole oil/water separation systems may be a way of dealing with the problem of sheen formation before the sheen is formed. These systems allow for oil extraction with only a fraction of the water. This lower produced water volume could potentially allow for either a more thorough treatment of produced water with existing equipment, or the use of the lower flow, higher efficiency systems. Research on this topic is currently underway with the Dept. of Chemical Engineering, Dalhousie University, Halifax, Nova Scotia.

Re-injection is a costly but effective alternative to produced water treatment. Dan Byers (ONDEO Nalco) indicated that in many parts of the world oil companies are being pressured towards a *zero discharge policy*, and re-injection appears to be the option of choice. He solidified this point by mentioning British Petroleum had just finished a series of re-injection wells in Mobile Bay, where proximity to shore prohibits produced water discharge. Re-injection still requires water treatment to reduce fouling and plugging, sometimes to a greater degree than for ocean discharge.

Dispersants

When oil is spilled at sea, a small proportion will be naturally dispersed by the mixing action caused by waves. Dispersants are used to accelerate the removal of oil from the surface of the sea by greatly enhancing the rate of natural dispersion by reducing surface tension. The development of modern dispersants began after the Torrey Canyon spill in 1967. Modern dispersants have been shown to be effective in oil slick breakup, however their effectiveness on sheens alone is questionable.

For a dispersant to be most effective it must be applied at the correct dispersant to oil ratio, as well as at the correct droplet size. A dispersant's efficiency is optimal when it is placed at the oil water interface; too large of a droplet will penetrate this interface, while too small droplets will remain on the oil surface. The use of dispersants on sheen may be difficult to optimize, or in the case of rapidly disappearing sheens, of little benefit.

Booms

Advances in boom technology and composition could renew their position for the containment and cleanup of hydrocarbon releases after the sheen has formed.

Mother Environmental Systems has released a new product "Mycelx" which when infused into booms or bilge pumps claims to be 100% effective at removing hydrocarbons (less than 1 ppb), although flow rates were not available. Earth Canada manufactures the only reusable hydrocarbon absorbent that can be incorporated into a boom, and later centrifuged and reused up to 100 times.

Typically booms are used more for the containment of an oil slick than its cleanup. However with the relatively minuscule amount of hydrocarbon needed to produce sheen, the absorbing capabilities of these new booms could both contain and remove the oil at the same time. As with dispersants, boom efficiency is dependent upon environmental

conditions. They do not perform well in winds over 15 knots, however such winds would likely reduce the need to deal with sheens. The cost effectiveness and technical issues of using booms on transient events like sheens also makes their use questionable.

Filters/Adsorption Media

A large variety of filters or membrane systems, including ultramembrane materials and filtration coalescers, capable of reducing hydrocarbon levels to industry standards have been proposed. However, issues regarding flow rates, regular maintenance, break through threshold, disposal, and water composition (solids, oil levels, salinity) are all detriments which in most cases will outweigh their usefulness for offshore platforms at the current time.

Adsorption techniques (e.g. organophillic clays, activated carbon, macro porous polymer extraction), while more costly, can also achieve very highly purified water. Regeneration or disposal of the media is required. These types of polishing technologies are limited to operations with low volumetric rates of produced water, i.e. under 1000 cu m per day (42 cu m/hr).

Skimmers

A number of companies market free floating skimming devices for cleanup after a slick has formed. These units vary in the rate at which they can remove oil from a surface, and the level of hydrocarbon remaining after their use. All skimmers reviewed rely on the density differential between oil/water, therefore they might require modification to remove sheens and would likely have to retrieve a significant layer of water underlying a sheen.

Sensing Equipment

Various companies market sensing equipment, which can detect everything from sheens to turbidity. Installing meters at various stages of the water treatment process to give real time indications of efficiency, may give insight as to where additional processes, retention times, or chemical injection need to take place. Sensors might also assist in detecting sheens forming on the ocean surface which are not visible to observers on the platform.

Discussion

Table 3 below indicates the characteristics and status of several of the technologies for use after API and parallel/corrugated plate separators.

The table shows why hydrocyclones and flotation are the most common methods for reverse emulsion treatment. Biological, filtration and adsorption media alternatives

require further development to overcome drawbacks and/or are too costly for high water rates.

Table 3: Selected Treatment Technologies Summary

Type	Removes	Pros/ Cons	Testing
Biological	* Removes biodegradable materials, including hydrocarbons, organics, H_2S, some metals, and in some conditions ammonia.	* Development needed before use offshore. * Is heavy and needs a lot of deck space. * Buildup of oil/iron may hinder biological activity. * Aeration may cause calcium scale to form. * Requires pre-treatment	* Not tested offshore, but in use onshore in California and Tjelbergodden.
Filtration	* Can remove particles, dispersed and emulsified oil. * Phenols, polar and dissolved compounds are poorly removed; ultramembrane technology requires further development.	* Small size, low weight and low energy requirements with high throughput rates. * Problems with regular maintenance and handling of hazardous waste. * Oil, sulfides or bacteria may foul membrane, which requires frequent cleaning.	* In use * Planned on Ekofisk to remove dissolved components
Adsorption Media	* Can remove fine droplets * Carbon used downstream of clay if necessary	* Can reduce hydrocarbons to very low levels. * Media eventually become spent and require disposal. * Limited to low water rates for economic reasons.	* In use
Steam stripping	* Possible to remove up to 85% of the dissolved components and 80% of the dispersed oil. * Can also remove benzene, toluene, naphthalene, phenanthrene, anthracene, pyrene and phenols. * H_2S and ammonia can be stripped but pH must be adjusted.	* Can be fouled by high oil content. * Risk of iron and calcium scales forming. * Generates an off-gas stream that may require treatment * Needs quite a bit of space, in practice better in cleaning small water volumes	* In use
Flotation Cells	* Removes dispersed oil > 20 microns	* High capacity. * Needs relatively long retention time (4-5 mins). * Must be used together with other cleaning technologies.	* In use

Type	Removes	Pros/ Cons	Testing
Hydro-cyclones	* Removes dispersed oil > 10 microns	* Can be connected in parallel and therefore high flow rate. * Variable effectiveness. * Not suitable for condensates. * Cleaning efficiency depends on the chemicals added in the process.	* In use
Centrifuge	* Removes dispersed oil > 2 microns	* Very efficient for dispersed oil removal. * Compact design. * Can handle variable flow. * High investment and operating costs. * High maintenance and energy consumption. * Vulnerable to sands and solids.	* In use

Interviews

Summary

Information was obtained from oil and gas industry personnel with operations or environmental experience in Canada's East Coast, the Gulf of Mexico, the North Sea and Australia (Timor Sea). Additional contacts were made with researchers/practitioners in the areas of spill response and oil and gas marine pollution and impacts and reference is made to documents relevant to subjects covered by the interviews. In most cases, direct references to individual respondents have not been divulged to allow for some level of anonymity.

Sheens were noted as widespread in the North Sea but rare at Hibernia. Treatment trains identified were similar to those described in the technology section (separators followed by air flotation, hydrocyclones, sometimes with chemical induced flocculation or proposed clay adsorption). Respondents observed more sheens where equipment was old or at full capacity, after solids discharge, when effluent discharge was near the surface, or were related to operational problems dealing with heavier hydrocarbons or high influent concentrations. The propensity of sheens to occur at higher discharge concentrations was acknowledged, as well as exceptions to this. Buoyancy due to temperature difference with the ocean off Canada's East Coast was suspected to favour sheen formation.

Sheen monitoring varied, but when sheens were identified, tended to triggered checks of treatment systems. Identification of sheens was contingent upon the time of day, weather and angle. No monitoring of particle size or suspended solids was done, although salinity

was regularly tracked by one company. Industry participated in studies upon benthos, e.g. mussels, and tested for metals, radioactive elements and toxicity periodically. One company was conducting an investigation of sheens which involved analyzing microlayer content and planned to correlate sheens with operational factors. The Department of Fisheries and Oceans had not found evidence of elevated bacteria levels surrounding platforms in Eastern Canada, perhaps indicating oil content in produced water discharges is not high enough to noticeably stimulate bacteria levels, and/or other mechanisms – dilution, dispersion, evaporation, sedimentation - dominate.

Several industry respondents felt thin sheens did not harm birds and were in any case, rapidly dispersed and biodegraded. Concerns over the short and long term impact of sheens upon birds nevertheless exist, although data on this is limited. Thresholds for acute effects have been determined in one spill model. Literature suggests that non-lethal impacts from large spills can have long term effects upon food sources and reproductive behaviour.

Results

Sheen Occurrence

With respect to sheen formation, responses from industry personnel as to sheen occurrence varied widely. Hibernia operations (Newfoundland) were not considered to be subject to sheens from produced water, while occasional sheens had been observed during Cohasset-Panuke (Nova Scotia) production in the 1990's where internal company targets were 25 ppm (1999 monthly average oil in water values averaged 21.5 ppm, standard deviation of 3.1 ppm). Sheens were the norm at many platforms in the North Sea, particularly where the treatment technologies may be dated and water volumes large. The corresponding average monthly limit was 40 ppm, although the industry as a whole averaged just under 22 ppm in 1999 (UKOAA). In the Gulf, sheens were more common in the 1990s, but were rare in the last five years, in part due to prohibitions against produced water discharge within coastal waters, and treatment systems designed and/or operated so as to meet stricter total hydrocarbons limits (29 ppm at the time). Another company's Gulf respondent noted they had not had a sheen for four years, and were cleaning produced water to levels below the current applicable regulatory limit of 20 ppm.

Sheen Causes

With respect to the causes of sheens, respondents agreed that sheen observations usually required calm seas, clear days and specific positioning of a viewer. Some were of the opinion that the nature of the associated hydrocarbon was a factor; i.e. heavy crude oil tending not to form sheens but rather mousses whereas condensates and medium crude oil spread more readily to form the requisite thin layer identifiable as a sheen. The buoyancy of higher temperature discharge water was thought to bring produced water to the ocean surface quickly, facilitating sheen formation.

An expert in the field of spill modeling, Deborah French McCay, commented that no information was published correlating produced water concentrations and sheen potential (Applied Science Associates, pers. comm., 2002). She had performed hydrocarbon fate modeling of produced water discharges, but it had yet to be validated against real data. Modeling of a bitumen – water emulsion spill was recently completed for the Bay of Fundy by French McCay.

Several of the informants expressed the view that while sheens were less likely at low concentrations, sheens could still occur at concentrations under 20 ppm. Inversely, high hydrocarbon concentrations (over 50 ppm) might not cause surface sheens. This difference in behaviour was attributed to the petroleum hydrocarbons being predominately dissolved rather than emulsified or dispersed.

Merv Fingas (Environment Canada, pers. comm., 2002) noted that visible sheens were "not an indicator of presence or absence of hydrocarbons ". Rather, they were "usually always present and...visible under certain conditions". He added that the higher the levels of volatile hydrocarbons and the less viscous the petroleum, the more likely the sheen was to be less than a micron and therefor not discernible to the naked eye. Moreover, weather conditions might prevent formation of the sheen on surface.

Sheen Monitoring and Reporting

With respect to sheen reporting to authorities, this depended upon whether the sheens were considered to be due to a mechanical failure or not. Because regulators regarded the appearance of sheens as indications of possible regulatory exceedances, internal records of unreported sheens were kept by most companies even if they determined a sheen was not due to "non-compliance".

Most respondents indicated their companies had protocols in place for characterizing sheens. Use of the "Thickness Appearance Rating Code" (TAR Code) developed by the Canadian Coast Guard and Environment Canada was cited. Software or other methods were used for estimating volumes of oil associated with sheens. In the Gulf of Mexico, all sheen volume was tracked and reported to the US Coast Guard. For instance, a 1997 summary (pers. comm., 2002) noted 22 sheen events adding up to approximately 1.6 US gallons of oil (approximately 6 L in total).

At those North Sea platforms where sheens are frequent, only sheens considered out of the ordinary by operations staff cause them to investigate treatment processes and other possible malfunctions (Ian Buchan, Talisman Energy, pers. comm., 2002). Such sheens might stretch a kilometer or more from the rig as a result of wind and currents. The usual, recurring "persistent" sheens started as small areas a few meters in diameter, becoming "snail trails" or fingers perhaps a few 100 meters long. These disappeared within an hour.

One Gulf respondent noted (pers. comm., 2002) that they periodically observed an oil "bubble popping on surface" to form a one or two foot diameter sheen. Eventually they

realized the sheens appeared several days after dumping sand from the dissolved air flotation unit into the scuppers, which channel rainwater into the discharge pipe. This underscores the importance of solids carryover as a probable contributor to sheen formation.

Testing for trace metals, naturally-occurring radioactive materials (NORM's) and toxicity (LC50) are conducted semi-annually or annually. No respondents currently test for suspended solids or could recall having done so in the past. As well, one company regularly measured for salinity. Since the total dissolved solids content (salinity) of the produced waters can often be very elevated resulting in significant density differences compared to seawater, this could be critical to sheen formation due to buoyancy effects, as noted previously.

Particle distribution measurements were cited by one respondent as having been carried out in the past in order to design or optimize equipment. This information was apparently not used to correlate with sheen observations. Rather, most operations relied upon total hydrocarbon analysis to evaluate produced water treatment system performance. A Canadian interviewee noted that technologies suitable to measure particle size distribution on the rig were considered expensive.

Jan Rusin, Environmental Manager for Talisman UK, revealed (pers. comm., 2002) that his company was currently analyzing microlayer samples to determine the composition of sheens, e.g. which fraction of hydrocarbons or which chemicals are accumulating on the surface. They were hoping to check theories that sheens are made up of fatty acids or well treatment chemicals. Next steps in their research program will be to monitor sheens when varying treatment processes, chemical injection, etc. Despite this example, Rusin argued that research and sheen minimization efforts were not directed at resolving sheens per se. They were a convenient observation that could indicate produced water treatment problems and so were monitored by both industry and government.

Technologies Used

Regarding the technologies currently used to treat produced water, all respondents cited the use of three phase separation vessels. In several installations, the separated oily water stream was fed to one or more hydrocyclones. Hydrocyclones were used because they were considered "best proven available technology," were lightweight and compact with a high throughput, had few moving parts and so were easy to maintain. They lend themselves to retrofits and are cost effective.

While hydrocyclones were noted as being very efficient during steady state conditions, their performance was more affected than other technologies during changing flows or flows outside of their design range. One respondent indicated that adjustments narrowing the water reject stream so as to lower the discharge oil concentration caused more oily water to be recycled back to the separators, thereby reducing the volume output and possibly changing the performance of the upstream process units.

In the Gulf of Mexico, one respondent noted that their operations beyond the mandatory reinjection distance from shore, used air flotation in keeping with Best Available Technology requirements. This technology can bring petroleum hydrocarbon concentrations to below 15 ppm. One company typically cleaned to 5 to 10 ppm oil using the flotation cells after primary two or three phase separation.

EnCana planned to use organophillic clay to polish produced water after hydrocycloning in their upcoming (Nova Scotia) deep Panuke gas project. Produced water volumes were expected to be lower than previous production in Cohasset-Panuke (estimates from the East Coast respondents were 600 to 3000 cu m per day, 25 to 125 cu m/hr), making this type of process economic.

One Gulf respondent noted that when he first started work in the Gulf, they had trouble meeting regulations, mainly due to the poor condition of equipment e.g. sand buildup in vessels, faulty control valves, and weirs not adjusted properly. Once they did initial maintenance on equipment and changed chemical products, they were able to meet regulations most of time. Preventative maintenance was key. In the platforms he was familiar with, the water rejected from the oil polishing separator (which used chemical to break water in oil emulsions) went to a flotation cell. Then depending on the type of oil, it went to an electrostatic precipitator. Sometimes clarifiers (using chemicals to promote flocculation) were also used.

They found condensates separated well, but heavy oils did not. Basic sediment and water (BS&W) targets were challenges with the heavy oil, more so than treatment of the reverse emulsions. Also, completion chemicals were blamed for making initial water-oil separation difficult. In his experience, poor separation at initial separators caused more oily water to require treatment, and therefore more loading of coalescers and flotation cells.

Currently they were working with a manufacturer testing out a prototype hydrocyclone that could be adjusted for efficient operation over a wider range of flows. They planned to use performance data e.g. flow and oil concentration as well as operating costs, including any savings in chemical inputs, to evaluate performance.

In the North Sea, Talisman Energy operators strive to be below 30 ppm (Ian Buchan, Talisman Energy, pers. comm., 2002). They sometimes managed to be less than 25 ppm, depending on the platform treatment train's age and loading. The North Sea platforms cited ranged from 8 to 25 thousand cubic meters of produced water per day (330 to 1040 cu m/hr). At an older platform, water coming out of the initial large high pressure separation vessels for well fluids ran through tilted plate separator in parallel with a more recently installed hydrocyclone. Sometimes gas flotation was used as well. Hydrocyclones were considered the most efficient and effective technology, in some cases capable of achieving 13 to 15 ppm concentrations. As part of upcoming upgrades to one old platform, an above surface discharge outlet was to be lowered.

Research into produced water composition, transport, fate and contaminant affect underway by the Canadian government attributes contaminant loading of the benthic zone and surface microlayer to flocculation reactions by hydrolysis metal precipitates in aerobic seawater (Natural Resources Canada). Dan Byers of ONDEO, quoted above, had observed this effect first-hand. He stated that sheen formation due to iron oxidation at several installations in the Gulf was reduced by lowering discharge outlets below the water surface. The problem was not entirely eliminated because receiving waters were still well oxygenated due to the shallow depths at the rig site. Fingas also noted that the discharge orifice design was important for sheen formation. Interviews indicated North Sea and Gulf platforms with shallow discharge depths were more likely to experience sheen formation. A North Sea environmental manager commented that while unaware of any companies using a high shear pump for the purpose of breaking up oil particles prior to discharge, it might be a tool to avoid sheen formation.

The Influence of Regulations and Future Trends

As part of new OSPAR commitments, there will be an added reduction in hydrocarbon discharges for North Sea countries. By 2006, each country must reduce ocean hydrocarbon discharges by 15%, using 2000 as the baseline. This will have to be done while mature fields continue to age and new production is brought on. Since some operations' discharge will be able to be reduced more easily than others will, Rusin, who also chairs the produced water committee of UKOAA, was encouraging development of a mechanism to allow pooled funds from various companies to be directed at those projects which would bring about the greatest decreases in oil discharge. There was already an informal system to trade flaring.

Moreover, Rusin noted that dissolved components were becoming more of an issue. Should limits for dissolved concentrations be introduced, they would need to use technologies such as membranes, exchange processes, and enhanced photo-oxidation

technologies. Dissolved concentration regulations, were they to come into effect, would undoubtedly encourage more reinjection in the future.

Environmental Effects

Lastly, the interviews touched briefly on environmental effects. No industry respondents were aware of research into environmental effects of sheens specifically. East Coast companies had participated in research on shellfish oil tainting from drilling muds/fluids. Water quality testing was also conducted around Canadian East Coast platforms to determine spatial and temporal variation in metals and hydrocarbons. The variation evaluated was very wide. A study involving analysis of hydrocarbons obtained from oiled seabirds on Sable Island was thought to be nearing publication. Reportedly the study found one percent of oiled birds had hydrocarbons which could be traced to Canadian East Coast production operations (Stephen Full, Encana Resources, pers. comm., 2002).

One Gulf of Mexico respondent felt evaporation and bioremediation limited the environmental impact of sheens. Patin (1999a) notes bioremediation rates are difficult to estimate since many factors are involved. Generally, it occurs most readily with alkanes and with warmer temperatures and where suitable substrates and nutrients were available. Hydrocarbon degradation has however been shown to adapt to low temperatures: a North Sea study measured biodegradation at temperatures as low as 2°C and calculated rates of 0.5 to 50 g/m3/d (Patin, 1999a). Sampling around the Panuke Platform sites, Thebaud Rig and Hibernia Gravity Base Structure in 2000 found no evidence of an impact upon microbial activity from "current" produced water discharge levels (Natural Resources Canada, 2001, p. 15). Reporting emphasized the fact that this might change with greater future production.

The Department of Fisheries and Oceans (DFO) concluded in a document providing advice on the Offshore Waste Treatment Guidelines review (March 2000) that the effects of chronic exposure of marine organisms to produced water were not known. They also expressed concerns over the tendency for produced water contaminants to concentrate in sediments and the surface microlayer of the sea.

The sheens observed by North Sea industry personnel, which on a calm sea slightly altered the shade of the ocean and smoothed it out, attracted seabirds. The birds, in one respondent's opinion, did not suffer ill effects from the very thin sheens.

The SIMAP model noted above uses 10 microns thickness (three times the upper boundary for the working definition of a sheen) for slicks over 230 m in diameter as the cut-off for lethal effects due to oiling (French et. al. 1996); for slicks smaller than this the threshold is 100 microns. This threshold is based on a review of literature, although the authors note, "[d]ata supporting the appropriate threshold thickness are very difficult to find" (1996, p. I4-41). The model relies on a study of eiders by Jenssen and Ekker (1991) which found lethal effects in the range of 200-500 ml, and a dose of at least 20 ml for an effect on metabolism. This is correlated to the behaviour of varying types of seabirds

(dabbling, aerial, surface, etc.), and movement through a surface layer of hydrocarbons to acquire a dose of oil given a slick or sheen's dimensions. The SIMAP model does not calculate any detrimental effects for sheens containing less than 20 ml of hydrocarbons. This volume is comparable to a 3 micron sheen with a diameter over 2900 m.

While the SIMAP model calculates only effects due to acute toxicity, various studies of impacts 10 to 11 years after the Exxon Valdez note that for some birds, there may be chronic, long term effects due to immune system suppression and/or behavioural changes which adversely affect reproduction and parenting. Contamination within food sources is also considered a possible pathway for chronic effects in bird population following large spills (Golet et. al., 2002; Ocean Studies Board et. al., 2003). Patin's review of the literature on seabird impacts suggests that populations affected will however have rebounded to "optimal" levels several years after an oil spill (1999b, p. 331). This observation may be highly dependent upon a widespread distribution of a particular species' population prior to a spill so that unaffected birds may repopulate an impacted area.

Tony Lock, of the Canadian Wildlife Service, agreed that there was a paucity of research as to the impact of sheens on birds (pers. comm., 2003). He expressed the view that correlations cannot be made from the size of a slick to the number of birds affected; rather location, timing and species were the important factors. Whether thin sheens were safe or not was not certain, but thicker sheens would likely be worse. Feather oiling, matting and ingestion due to preening might still be detrimental from oils picked up from a thin sheen. Lock emphasized that an agreed upon protocol for responding to sheens – e.g. treatment with dispersants, breaking up by agitation, etc. – should be developed.

DISCUSSION

Sheen Formation

The theory behind the formation of sheens is reasonably well understood. The prediction of when they will appear is, however, less well understood. This lack of understanding is caused by the many factors that can influence when sheens are formed or at least when they are visible. As one researcher suggested, sheens likely form frequently but are often invisible to the naked eye due to their thickness. Interviewees from the East Coast alluded to the difficulty of detection by viewers due to their physical location with respect to the ocean surface.

With such a variety of factors, ranging from ocean temperature and turbulence, to droplet size, to hydrocarbon type, to emulsifying agents, involved in sheen formation, it is problematic to evaluate which are the primary sheen causing factors. The one factor that stands out is the presence of hydrocarbon in the disposal water.

Even the presence of hydrocarbon in produced water is not a good measure of sheen formation potential. Quantities below regulated or industry standards (e.g., the 15 ppm MARPOL 73/78 limit used in the shipping industry) can still produce sheens on occasion. Still, higher oil-in-water concentrations would be associated with a greater tendency to have sheens form, all other factors being equal. Thus, the measurement of petroleum hydrocarbon content is still the best measure of the potential for sheen formation.

It is interesting to note the interview comments regarding older equipment having a greater tendency to produce sheens. As noted by one operator, old equipment was associated with a higher solids carry over and produced noticeable sheens.

The issue of solids and emulsifiers is also of interest. Traditionally oil in water values increase if there are a significant amount of solids present. These solids can include produced sands and silts and iron. The iron is normally a corrosion by-product. Measurement and monitoring of solids is likely another useful determinant of sheen formation potential.

Clearly, the primary cause of sheen formation is oil carry over. This is a direct factor of retention time, hydrocarbon type and emulsifying agents. If these factors as well as the amount of oil present in the water can be reduced or altered, sheens will be less likely to form.

Treatment Technology

The technology review did not identify a large number of new technologies for sheen prevention. The current technology of gravity separation, chemical treatment, flocculation and the hydrocyclone are well accepted, widely used and reasonably effective.

If there is a trend or trends in technology advancement it tends to be in the refinement of existing technology. Notably there is work underway to improve the performance of hydrocyclones. As well, new air flotation units are also being put into use. Technology that needs additional consideration and development includes biodegradation and filters.

In theory, biodegradation of small quantities of hydrocarbon in produced water should be relatively straightforward. Crude oils are well known to biodegrade. Bioreactors should be able to degrade hydrocarbon in a matter of minutes. The questions for produced brines will pertain to the retention times and size of vessels needed to be effective. As well, bioreactors must be designed to be able to accommodate increasing water volumes as producing wells age. It should also be noted that biodegradation is usually a low cost treatment option.

Because of the possibility that solids are a cause of oil carry over and therefore, are indirectly a cause of sheen formation, the possibility of solids removal should be reviewed. The simplest method of solids removal is filtration. Filtration is proven established technology for solids removal. The problem with filtration is that filters do not work effectively with even small quantities of hydrocarbon, particularly membrane filters. This is an area of technology that could be developed with more research.

The use of dispersents and booms was also evaluated as a possible "end-of-pipe" remedy for sheens. Both dispersents and booms could prove useful in treating sheens if the sheen was of a size or character that made it a threat to the environment. As "end-of-pipe" solutions, they are less useful then the prevention tools already in use or being developed. Agitation prior to discharge, or after sheens occur, is an option that has not been evaluated but which may warrant serious consideration.

Dispersants are also controversial and may not have the desired effect. Booms are costly, difficult to deploy and also have disposal issues associated with them. In general these technologies only have application in the most severe instances.

Interviews

There are a number of interesting observations that can be gleaned from the interviews.

The first is that although sheens are tracked on an informal basis, no real tracking is done. As well, although oil-in-water values are monitored, they are not related back to sheen formation. Other factors, such as suspended solids, which could impact on the formation of sheens, are not monitored at all.

There are numerous anecdotal observations on sheens, but little or no actual measured data. These observations pertain to size and frequency of sheens as well as correlations to equipment age and other factors. In some locations sheens are a frequent occurrence. In others they are a rarer and very transient event. Without more rigorous observations it is difficult to obtain a picture of the impacts if any from sheen formation.

Interviewees clearly indicated that existing technology can be made to work to reduce oil carry over and therefor sheen formation, depending on its age and the age of the associated equipment on the producing platform. New technology, such as bioreactors, would be of interest if it can be designed to fit on production platforms and can be demonstrated to be cost effective.

Few of the interviewees knew of any research into the impacts of sheens specifically. Although there is some speculation as to potential impacts and some information on effects on birds, no real studies have as yet been completed which address the long term impact of sheens. There is, however, certainly an aesthetic impact when sheens are visible.

It should be noted that although sheens can be large, they are also often very small. It does not take a significant amount of oil to produce a sheen. Indeed, one American interviewee (pers. comm., 2002) noted that in one year 22 sheen events were reported. These were estimated to represent a total of 1.6 US gallons (approximately 6 L) of petroleum hydrocarbon, as noted previously. This is an average of 270 mL per sheen. Given the biodegradation rates documented for hydrocarbons in cold seas and other mechanisms such as evaporation and dispersion, it is difficult to surmise that there is a significant impact from sheens. Acute impacts to seabirds may be limited to slicks and broad sheens where birds are able to pick up an appreciable amount of hydrocarbon, which limited research suggests may be at least 20 mL for adverse effects, and over 200 mL for lethal effects. Circumstances (location, weather, time of year, species) will affect the severity and extent of the impact. Assuming sheens are limited in size and duration and do not affect large parts of key foraging areas, impacts to birds may be slight. Further research into seabird impacts is desirable.

CONCLUSIONS AND RECOMMENDATIONS

The formation of sheens resulting from the disposal of produced water from offshore gas and oil production is a well-documented occurrence. Less well documented is the cause and prevention of such sheens.

Sheens are caused by a variety of factors. The most obvious is the carry over of petroleum hydrocarbon in the produced water. Other factors include weather, sea water temperature, hydrocarbon type and emulsifying agents. Of these factors the only ones controlled by the operator are hydrocarbon content and the emulsifying agents, particularly solids.

Equipment designed to remove petroleum hydrocarbons from produced brines is reasonably effective. Although new technology, particularly biotechnology and new filters are worth pursuing, they must be shown to be technically successful and cost effective.

Although sheen treatment technologies such as booms and dispersants may be useful in severe cases, pollution prevention equipment such as that in use is preferred.

The impacts of these very small volumes of oil is also unclear and primarily related to visual impacts. Impacts upon birds in particular are dependent upon timing, location and species involved.

Based on the observations and conclusions in this report the following recommendations are made:

1. Sheen production is not systematically monitored and correlated to carry-over of petroleum hydrocarbons in the produced brines. It is recommended ESRF work with various Canadian offshore operators to institute a three-month program to evaluate the frequency and significance of sheens. The proposed monitoring program should include reporting of (a) the estimated size of the sheen, (b) the concurrent concentration of petroleum hydrocarbons in the discharge produced brine; (c) the influence of trace metals within the brines on the visualization of the sheens and (d) the concentration of the total suspended solids in the produced brine.
   Alternative analytical techniques should be trialed to determine if their results for petroleum range hydrocarbons correlate better with the propensity of produced water to produce sheens. It is suggested that existing on-board weather/bird/wildlife observers could be readily trained to check for sheen formation and to correlate observations with other data. It may also be necessary for the rig operators to augment their existing discharge monitoring activities.

2. The ecological impact of sheens is not well understood. Further, when sheens are not apparent, hydrocarbon concentrations in the surface

microlayer may be elevated. It is recommended that a study of the environmental impacts of sheens, particularly impacts to seabirds and plankton within the upper 1 cm surface layer, should be completed. Issues to be evaluated should include effects on seabirds of low-level oiling of feathers, interruption of feeding, and scope for growth. The results of such studies would assist decision-makers with respect to imposing management controls on sheen formation and the concurrent discharge of petroleum hydrocarbons within produced waters.

3. Sheen formation is attributed to the presence of petroleum hydrocarbons within discharges of produced waters, in combination with key physical and chemical conditions. It is recommended that ESRF work with industry to (a) evaluate and implement new technologies for the removal of petroleum hydrocarbons from produced brines, including bioremediation and filtration and (b) evaluate and implement methods of discharging produced waters in such a manner as to impede the formation of sheens (e.g. by imparting more energy during discharge).

REFERENCES CITED AND SELECTED BIBLIOGRAPHY

Alaska Department of Environmental Conservation, Division of Spill Prevention and Response, Prevention and Emergency Response Program. *Situation Report: Unocal King Salmon Platform*. December 2001.

_____. *Situation Report: East Cameron 60*. N.d.

Advisory Committee on Protection of the Sea. **Annual Survey of Reported Discharges Attributed to Vessels and Offshore Oil & Gas Installations operating in the United Kingdom Pollution Control Zone**. For United Kingdom Maritime and Coastguard Agency. 2000.

Allen, Thomas O. and Aplan P. Roberts. **Production Operations: Volume 2.** Fourth Edition. Tulsa, Oklahoma: Oil & Gas Consultants International, 1993 (1978).

American Public Health Association, American Water Works Association, Water Environment Federation. **Standard Methods for the Examination of Water and Wastewater**. 18th Edition. 1992.

Antunes do Carmo and M. Costa. *Modeling oil spill evolution in estuaries and coastal regions*. **Oil & Hydrocarbon Spills II: Modeling, Analysis and Control**. Ed. by G..Rodriguez et. al. Southampton, Boston: WIT Press, 2000 (63-72).

Arnold, Ken and Maurice Stewart. **Surface Production Operations, Volume 1: Design of Oil-Handling Systems and Facilities**. Second Edition. USA: Butterworth-Heineman, 1999 (1989).

Australian Maritime Safety Authority. *The Effects of Maritime Oil Spills on Wildlife including Non-Avian Marine Life*. N.d. [Accessed February 26, 2003].

Ayers, Robert C. and Michael Parker. **Produced Water Waste Management**. Technical Report prepared for Task Force of the Environment sub-committee of the Canadian Association of Petroleum Producers (CAPP) East Coast Committee. CAPP, August 2001.

Bragg, J.R. and Yang, S.H. *Clay-Oil Flocculation and Its Role in Natural Cleansing in Prince William Sound Following the Exxon Valdez Oil Spill*. **Exxon Valdez Oil Spill: Fate and Effects in Alaskan Waters**. ASTM STP 1219. Ed. by Peter G. Wells, James N. Butler, and Jane S. Hughes. Philadelphia: American Society for Testing and Materials, 1995 (178-214).

Branto, R. *Principles for the Separation of Oil Drops from Water in Gravity Type Separators*. **Oil in Freshwater: Chemistry, Biology, Countermeasure Technology.** Vandermeulen, John H. and Steve E. Hrudey (ed.). New York, NY: Pergamon Press, 1987 (431-442).

Buchan, Ian. Environmental Advisor, Talisman Energy. Personal communication. 17 December 2002.

Byers, Dan. Representative, ONDEO Nalco. Personal communication. October and December 2002.

Canada-Newfoundland Offshore Petroleum Board. **Annual Report 2001-2002**. 16 May 2002.
_____. **Annual Report 2000-2001**. 18 May 2001.
_____. **Annual Report 1999-2000**. 23 May 2000.

Canada-Nova Scotia Offshore Petroleum Board. **Annual Report 2000-2001**. 30 June 2001.
_____. **Annual Report 2000-2001**. 19 June 2000.

Canadian Coast Guard. Spill database. On-line records as of August 2002.

Dunstan, A.E., A.W. Nash, B.T. Brooks, and H. Tizard. **The Science of Petroleum.** Volume II. Toronto: Oxford University Press, 1938.

Dykes, Greg. Worldwide Environment, Health and Safety Manager, Marathon Oil Company. Personal communication. 17 December 2002.

Fingas, Mervin. Senior Research Scientist, Environment Canada. Correspondence. 16 December 2002.

Fingas, Mervin, Ian Bier, Mark Bobra and Sandra Callaghan. *Studies on the Physical and Chemical Bahaviour of Oil and Dispersant Mixtures.* **Proceedings of the Twelfth Biennial Conference on the Prevention, Behavior, Control, and Cleanup of Oil Spills** (San Diego, California March 4-7, 1991).

Fiocco, R. J. and Lewis, A. *Oil Spill Dispersants.* **Pure Applied Chemistry**. Vol. 71, 1999 (27-42).

Department of Fisheries and Oceans (DFO), Canada. *Scientific Considerations and Research Results Relevant to the Review of the Offshore Waste Treatment Guidelines: Scientific Advice from DFO Atlantic Zone to DFO Senior Management.* Ed. by P.J. Cranford. 26 March 2001.

Ford, D.L. *Technology of Removal of Hydrocarbons from Surface and Groundwater Source.* **Oil in Freshwater: Chemistry, Biology, Countermeasure Technology**, op.cit., (413-430).

French, D., M. Reed, K. Jayko, S. Feng, H. Rines, S. Pavignano, T. Isaji, S. Puckett, A. Keller, F.W. French III, D. Gifford, J. McCue, G. Brown, E. MacDonald, J. Quirk, S. Natzke, R. Bishop, M. Welsh, M. Phillips and B.S. Ingram. *The CERCLA type A natural resource damage assessment model for coastal and marine environments (NRDAM/CME), Technical Documentation, Vol. I – Model Description.* Final Report, submitted to the Office of Environmental Policy and Compliance, U.S. Dept. of the Interior, Washington, DC, April, 1996, Contract No. 14-0001-91-C-11.

French McCay, D.P. *Development and Application of an Oil Toxicity and Exposure Model, OilToxEx.* **Environmental Toxicology and Chemistry**. Vol. 21, No. 10, September 2002 (in press).

_____. Consultant, Applied Science Associates, Inc. Personal communication. 10 December 2002.

French McCay, D.P. and James R. Payne. *Model of oil fate and water concentrations with and without application of dispersants.* **Proceedings of the 24th Arctic and Marine Oilspill (AMOP) Technical Seminar** (Edmonton, Alberta, Canada, June 12-14, 2001). Environment Canada (611-645).

French McCay, D.P. and Nicole Whittier. **Modeling Assessment of Potential Fates and Exposure for Orimulsion and Heavy Fuel Oil Spills.** Manuscript. Narragansett, Rhode Island: Applied Science Associates, Inc., 2002.

Fudge, Neva. *Oil spills and Seabirds: Assessing the Value of the Rehabilitation of Oiled Birds.* Essay. Atlantic Cooperative Wildlife Ecology Research Network (ACWERN), n.d. [Accessed February 26, 2003.]

Full, Stephen. Environmental Advisor, EnCana Resources. Personal communication. 6 December 2002.

Golet, Gregory H. et. al. *Long-term direct and indirect effects of the 'Exxon Valdez' oil spill on pigeon guillemots in Prince William Sound, Alaska.* ***Marine Ecology Progress Series.*** Vol. 241, 2002 (287-30).

Grisolia-Santos, D. and M.L. Spaulding. *The influence of oil particle size distribution as an initial condition in oil spill random walk models.* **Oil & Hydrocarbon Spills II: Modeling, Analysis and Control**, op. cit. (19-27).

Hoffman, E.J. and J.G. Quinn. *Chronic Hydrocarbon Discharges into Aquatic Environments: Municipal Treatment Facilities.* **Oil in Freshwater: Chemistry, Biology, Countermeasure Technology**, op.cit., (97-113).

Hrudey, S.E. and S. Kok. *Environmentally Relevant Characteristics of Oil-in-Water Emulsions.* **Oil in Freshwater: Chemistry, Biology, Countermeasure Technology**, op.cit., (58-70).

International Association of Oil & Gas Producers (OGP). *Aromatics in produced water: occurrence, fate & effects, and treatment.* Report No. 1.20/324. OGP. January 2002.

Jackson, George F., Eugene Humes, Michael J. Wade and Milton Kirsch. *Oil Content in Produced Brine on Ten Louisiana Production Platforms.* Project Summary, submitted to the U.S. Environmental Protection Agency, Research and Development, Municipal Environmental Research Laboratory, Cincinnati Ohio, Oct. 1981. EPA-600/S2-81-209.

John Parsons Associates Biological Consultants. *Oil based Drilling Muds Environmental Monitoring Program at Cohasset: Shellfish Tainting Study – 1993 to 1999 Program Results.* Prepared for PanCanadian Resources, Halifax. Dartmouth: December 1999.

Larsen, P.T. et. al. *Environmental spill modeling and risk assessment of Orimulsion 400 and Heavy Fuel Oil.* **Oil & Hydrocarbon Spills II: Modeling, Analysis and Control**, op. cit. (3-10).

Lee, R.F. *Agents Which Promote and Stabilize Water-in-Oil Emulsions.* **Spill Science & Technology Bulletin**. Vol. 5, No. 2: 1999 (117-126). Abstract.

Lock, Tony. **Marine Issues Biologist, Canadian Wildlife Service – Atlantic Region**. Personal communication. 24 February 2003.

Lu, Benjamin C.Y. and Jiri Polak. **A Study of the Solubility of Oil in Water**. Report EPS-4-EC-76-1. Environmental Protection Service, 30 March 1973.

Lunel, T. *Understanding the Mechanism of Dispersion through Oil Droplet Size Measurement at Sea.* **The Use of Chemicals in Oil Spill Response**. ASTM STP 1252. Ed. by Peter Lane. Philadelphia: American Society for Testing and Materials, 1995 (240-298).

MacKay, D. *Chemical and Physical Behaviour of Hydrocarbons in Freshwater.* **Oil in Freshwater: Chemistry, Biology, Countermeasure Technology**, op.cit., (10-21).

Mccain Jr., W.D. **The Properties of Petroleum Fluids** – Module 1. Videocassette. Society of Petroleum Engineers, 1983.

Ming Li and Chris Garrett. *The Relationship Between Oil Droplet Size and Upper Ocean Turbulence.* **Marine Pollution Bulletin**. Vol. 30, No. 12, 1998 (961-970).

Miyahara, S. *Formation of Water-In-Oil Emulsions.* **Oil in Freshwater: Chemistry, Biology, Countermeasure Technology**, op.cit., (71-84).

National Energy Board, Canada-Newfoundland Offshore Petroleum Board, Canada-Nova Scotia Offshore Petroleum Board. **Offshore Waste Treatment Guidelines**. 7 June 2002.

Natural Resources Canada, Program of Energy Research and Development. *Program at Objective Level (POL) Annual Report 2000-2001 – Objective 1.2.4: Regulatory Requirements for Offshore Drilling and Production Wastes, Assessment of Cumulative Effects, and Remediation of Accidental Offshore Discharge and Spills.* Natural Resources Canada, May 2001.

Nordvik, A.B.; J.L. Simmons, K.R. Bitting, A. Lewis, T. Strocm-Kristiansen. *Oil and water separation in marine oil spill clean-up operations.* **Spill Science & Technology Bulletin**. Vol. 3, no. 3, 1996: (107-122). Abstract.

Ocean Studies Board (OSB), Marine Board (MB), Transportation Research Board (TRB). **Oil in the Sea III: Inputs, Fates, and Effects**. National Academies Press (NAP), 2003.

Oiled Wildlife Care Network. *Oiled Wildlife Response in California*. Los Angeles: University of California – Los Angeles (UCLA), n.d. [Accessed January 2003]

Osamor, Chukwuka Azubuike. **Oil slick dispersal mechanics: spreading, dissolution, and chemical dispersion**. University Microfilms International. Ann Arbor, Mich. 1981 (thesis).

OSPAR Commission for the Protection of the Marine Environmental of the North-East Atlantic. *Draft OSPAR Background Document Concerning Best Available Techniques and Best Environmental Practice for the Management of Produced Water from Offshore Installations*. 17 April 2002a.

_____. *Meeting of the Offshore Industry Committee (OIC): Cleaning techniques for produced water tested by the Norwegian offshore industry*. OIC 02/3/22-E (Agenda Item 3). Cadiz: 11-15 February 2002b.

O'Sullivan, A.J. and T.G. Jacques. *Effects of Oil in the Marine Environment: Impact of Hydrocarbons on Flora and Fauna*. Community Information System for the Control and Reduction of Pollution: Impact Reference System. Brussels: European Commission, Directorate General Environment, Civil Protection and Environmental Accidents, n.d. [September 2002].

Palczynski, R.J. *Model Studies of the Effect of Temperature on Spreading of a Crude Oil on Water* in **Oil in Freshwater: Chemistry, Biology, Countermeasure Technology**. op.cit., (22-30).

Parent, R. and C. Lau. **Summary of Spill Events in Canada (1984-1995)**. Environment Canada.

Patin, Stanislav. **Environmental impact of the offshore oil and gas industry**. Trans. by Elena Cascio. East Northport, New York: Ecomonitor Publishing, 1999a.

_____. **"Economic Development and the Environment" on the Sakhalin Offshore Oil and Gas Fields II.** Slavic Research Center, Hokkaido University, 1999b.

Plosz, Gavin. Environmental Services Representative, Enviro-Test Laboratories. Personal communciation. 25 March 2003.

Ross, Cal. Senior Environmental Specialist, Exxon Mobil Canada East. Personal communication. 16 December 2002.

Rusin, Jan. Environmental Manager for United Kingdom, Talisman Energy. Personal communication. 18 December 2002.

Soares dos Santos, A. and P. Daniel. *Oil spill modeling near the Portuguese coast* in **Oil & Hydrocarbon Spills II: Modeling, Analysis and Control**. op. cit. (12-27).

Taylor, Dave. Consulting Ecologist, D.G. Taylor Inc. Personal communication. 13 December 2002.

Tedeschi, E. *Booms*. **Pure Applied Chemistry**. Vol. 71, 1999 (17-25).

United Kingdom Offshore Operators Association. **Environmental Report 2000**. UKOAA, n.d.

US Code of Federal Regulations. *Title 40--Protection of Environment, Chapter I—Environmental Protection Agency (Part 435—Oil and Gas Extraction Point Source Category)*. [As of August 2002].

US National Oceanic and Atmospheric Agency. Spill Database. [As of August 2002]

Vershueren, Karel. **Handbook of Environmental Data on Organic Chemicals**. 3rd Edition. USA: Van Nostrand Reinhold, 1996.

Volckaert, F.A.M., G. Kayens, R. Schallier, T.G. Jacques. *Aerial Surveillance of Operational Oil Pollution in Belgium's Maritime Zone of Interest*. **Marine Pollution Bulletin**. Vol. 40, No. 11, Nov. 2000: (1051-1056). Abstract.

Weintritt, Donald J., Nida S. Qaisieh and Gordon H. Otto. *How to Improve Accuracy in the EPA Static Sheen Test*. **Oil Gas J**. 3 May 1993 (77-82).

Wells, Peter G., Robert A. Duce, Michael E. Huber. *Caring for the sea – accomplishments, activities and future of the United Nations GESAMP (the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection)*. **Ocean & Coastal Management**. 45, 2002 (77-89).

Williams, Urban. Environment Lead, Petro-Canada. Personal correspondence. 18 December 2002.

Wills, Jonathan. **Muddied Waters: A Survey of Offshore Oilfield Drilling Wastes and Disposal Techniques to Reduce the Ecological Impact of Sea Dumping**. Abstract. 25th May 2000.

_____. Personal communication. 19 September 2002.

physics/bu.edu/py105
picea.sel.uaf.edu
wine1.sb.fsu.edu/chm1045
www.api.org
www.aquatechnologies.com/technology/treatrslts.htm
www.amsa.gov.au
www.axsia.com/
www.biologylessons.sdsu.edu/classes/lab1/lab1.html
www.bakerhughes.com/bakerpetrolite/oilgas/water_clarifiers.htm
www.capp.ca
www.cfertech.com/Core/Expertise/PT%20Proj/PT_proj_DHOWS-JIP.htm
www.cnopb.nfnet.com
www.cnsopb.ns.ca
www.dfo-mpo.gc.ca/oceanscanada
www.earthcanada.com/00_eng/main.html
www.ec.gc.ca
www.elsevier.com
www.environmental-center.com/articles/article1057/article1057.htm
www.epa.gov
www.europa.eu.int/comm/environment
www.ilpi.com/genchem
www.imo.org
www.ionics.com/products/division/instruments/oil-on-water/leakwise.htm
www.mas.ncl.ac.uk
www.mcga.gov.uk
www.mun.ca
www.mycelx.com/
www.nap.edu
www.natcogroup.com
www.noaa.gov
www.nrc.ca/cisti
www.offshore-environment.com
www.offshore-technology.com/contractors/separation/minox/

www.oilandgas.org.uk/issues/drillcuttings/rdp2-5ab.htm
www.osradp.lsu.edu
www.people.virginia.edu
www.pro-gear.ca
www.ramsorb.com
www.sft.no/arbeidsomr/vann/petroleum/Norway_cleaning_techniques.pdf
www.spilldepot.com/
www.spillsupply.co.za/lamor%20products.htm
www.src.sk.ca
www.state.ak.us/dec/dspar/perp
www.vetmed.ucdavis.edu/owen/Summary%20pdfs/Ch.3.pdf
www.ukooa.co.uk
www.wedgewoodtech.com